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Tetradentate Cyclometalated Platinum(II) Complexes for Efficient and Stable Organic Light-Emitting Diodes

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Abstract

As one of the most important phosphorescent emitters, tetradentate cyclometalated platinum(II) complexes have attracted much attention in recent years, because of the high luminescent efficiency, emission spectra, and color tuned easily, especially for the development of high-efficient deep-blue and “pure” blue emitters and single-doped white organic light-emitting diodes (OLEDs). Also, some platinum(II)-based OLEDs exhibited superior operational stability, indicating their potentials in full-color display and solid-state lighting applications. In this chapter, we will introduce the recent advances of the tetradentate cyclometalated platinum(II) complexes, including pyrazole, *N*-heterocyclic carbene, imidazole and pyridine-based complexes, molecular design, photophysical properties, and some of their device performances.

Keywords: platinum complex, tetradentate, OLED, blue emitter, phosphorescence, operational lifetime

1. Introduction

In the 1960s, the first organic electroluminescent spectrum was reported from the crystal of anthracene [1]. In 1987, Tang and VanSlyke from Eastman Kodak Company successfully demonstrated an efficient and practical organic light-emitting diode (OLED) employing tris (8-hydroxyquinolino)aluminum (Alq₃) as a fluorescent emitter [2]. After that, OLEDs began to attract more and more attention in both academic and industrial researches for their potential applications for full-color displays and solid-state lighting industry.

From the spin statistics, it is well known that the singlet and triplet in the electrogenerated excitons are 25 and 75%, respectively [3]. As a result, OLEDs using fluorescent emitters, which

emit from the singlet excited state, can achieve a peak internal quantum efficiency (IQE) only 25%. However, if heavy metal ion is incorporated into the organic ligand, phosphorescent emitters can break the spin-forbidden reactions, and fast intersystem crossing (IC) from singlet to triplet state can occur owing to the strong electron spin-orbit coupling (SOC); thus, heavy metal complexes have the potential to harvest both the electrogenerated singlet and triplet excitons and achieve 100% IQE. In 1998, Forrest and Thompson et al. and Che et al. first reported the electrogenerated phosphorescent platinum(II) [4] and osmium(II) [5] complexes, respectively. Afterward, more heavy metal complexes were found to be used as efficient phosphorescent materials, like iridium(III), ruthenium(II), palladium (II), rhodium (III), gold(III), and so on, and some reviews about these complexes have been published [6–18]. Among them, iridium(III) complexes have been most widely studied. Green and red phosphorescent iridium(III) emitters developed by Universal Display Corporation (UDC) have been successfully commercialized due to their superior efficiency and long operational lifetime. OLED display doped these emitters that have been adopted for several types of high-end personal electronics, such as Samsung Galaxy, LG OLED television, Apple smart watch, and iPhone X. Compared with the liquid crystal display (LCD), OLED display have many outstanding merits, such as low-cost fabrication methods, high color quality, and high-luminance efficiency and also many advantages of low power consumption, wide-viewing angle, wide temperature range, fast response, etc [19, 20]. Thus, OLED has been widely considered as the next generation of full-color display and solid-state lighting technologies.

The development of high efficient and stable phosphorescent emitters is of the most importance for the development of OLEDs and their application. Although thousands of phosphorescent heavy metal complexes have been reported, the emitters can meet the requirement of commercialized displays, which are extremely rare. Now, considerable challenges still remain, for example, the development of efficient green and red emitters with high color quality, especially for the efficient and stable blue and deep-blue phosphorescent emitters. Much of the previous research work and the commercialized phosphorescent emitters mainly focused on the iridium(III) complexes. However, in the past few years, many reports demonstrated that the photophysical properties and device performances of the platinum(II)-based emitters could compare with or even superior to the iridium(III) ones in many aspects [16]. Also, some unique properties were found for some of the platinum(II) complexes, like narrowband emissive spectra, efficient deep-blue emitting, and excimer formation for single-doped white OLEDs [16]. These properties enable the platinum(II) complexes to have potential to be utilized in commercialized displays.

Taking into account the rapid development and unique properties of the platinum(II) complexes, in this chapter, we will mainly highlight their recent progress regarding their molecular design, photophysical properties, and device performances, especially for the tetradentate ones with cyclometalating ligands based on pyrazole, *N*-heterocyclic carbene, imidazole, and pyridine derivatives.

2. Why employ tetradentate ligands?

Because of the relatively long luminescent lifetime and poor quantum efficiency (φ), platinum(II) complexes were historically not considered as ideal emitters. However, through

judicious molecular design, bidentate platinum(II) complex can also emit strongly with lifetime in microsecond region, such as (ppy)Pt(acac) (**Table 1**) (1) [21]. Due to dsp^2 hybrid orbitals that are adopted for the Pt(II) ion, the molecular configuration of the platinum(II) complexes is square planar. Consequently, bidentate platinum(II) complexes are usually very flexible, and the excited state energy can be consumed by many nonradiative decay pathways, like molecular distortion and bond vibration. This can be proven by the emission spectrum of (ppy)Pt(acac) (**Figure 1**), which exhibits a strong vibrational transition $v_{0,1}$ at 518 nm, and, also, the nonradiative decay rate is 4.5 times faster than that of the radiative decay rate in CH_2Cl_2 solution at room temperature (RT).

The rigidity of the molecule would be enhanced if the tridentate ligand was employed, which could suppress the nonradiative decay pathway and favor to increase the ϕ . Therefore, Pt(dpyd)Cl (**2**) has a weaker vibrational transition $v_{0,1}$ at 523 nm than that of (ppy)Pt(acac), and the ϕ is increased to 60% [22]. However, the other monodentate ligand was needed to ensure the neutrality of the molecule. Furthermore, the chloride ion is a weak coordination ligand. All these would disfavor the molecular thermal and electrochemical stabilities. Therefore, more rigid and stable ligands are needed for further development of efficient and stable platinum(II)-based phosphorescent emitters.

Judicious tetradentate ligand design could provide rational coordination sites to the platinum(II) ions and maintain the square planar configuration, which are also of benefit to the material synthesis with high metallization yields. Most importantly, tetradentate platinum(II) complexes would have more rigid molecular configuration and improved photophysical and chemical properties. For example, the ϕ of the phenoxyl-pyridine (popy)-based complex PtOO3 [16, 23] could be up to over 80% in CH_2Cl_2 solution and be achieved to nearly unity in rigid PMMA matrix. If more rigid carbazolyl-pyridine was incorporated and served as ancillary ligand, the ϕ could be further improved to 100% yield even in CH_2Cl_2 solution for complex PtON3. Furthermore, tetradentate platinum(II) complexes could be easily modified to improve their photophysical and chemical properties through changing ligand's conjugation degree, utilizing different coordination atoms, adopting various linking groups, or forming five- or six-membered chelates. Thanks to the continuous efforts of the scientific community, many efficient and stable platinum(II) complexes had been developed, making them serve as ideal phosphorescent emitters for OLED applications.

Comp.	In CH_2Cl_2 at RT					In PMMA at RT	
	λ_{max}/nm	$\phi/\%^a$	$\tau/\mu s$	$k_r/10^5 s^{-1}$	$k_{nr}/10^5 s^{-1}$	$\phi/\%$	$\tau/\mu s$
1 [21]	484	15	2.6	0.6	3.3	53	6.0
2 [22]	490	60	3.8	1.6	1.1	73	5.7
3 [16, 23]	512	83	2.0	3.2	1.8	97	4.5
4	520	100 ^b	4.2 ^b	2.4	0.0	—	—

^aAbsolute quantum efficiency.

^b ϕ and τ were measured in a solution of 2-MeTHF.

Table 1. Photophysical properties of the bidentate, tridentate, and tetradentate platinum(II) complexes.

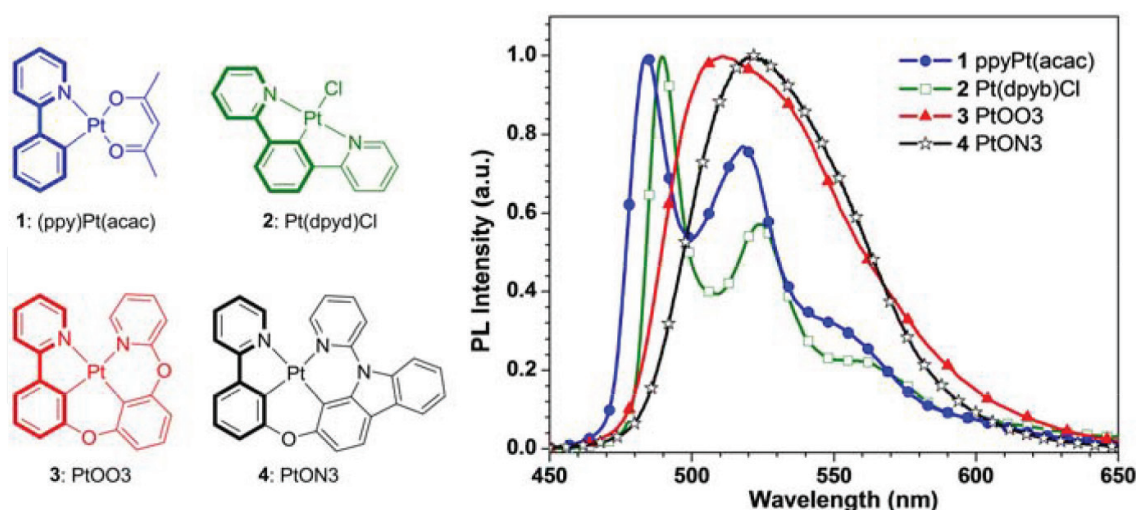


Figure 1. Molecular structures of (ppy)Pt(acac), Pt(dpyd)Cl, PtOO3, PtON3, and their PL spectra in CH_2Cl_2 solution (adapted with permission) [23].

3. Pyrazole-based tetradentate platinum(II) complexes

Because of electron-donating character and relatively weak π -conjugation ability of the nitrogen atom at the 2-position of the pyrazole ring, 1-phenyl-pyrazole (ppy) and its derivatives are widely incorporated into the tetradentate platinum(II) complexes (**Figure 2**). These complexes usually have a high LUMO energy level, making them suitable for developing green to

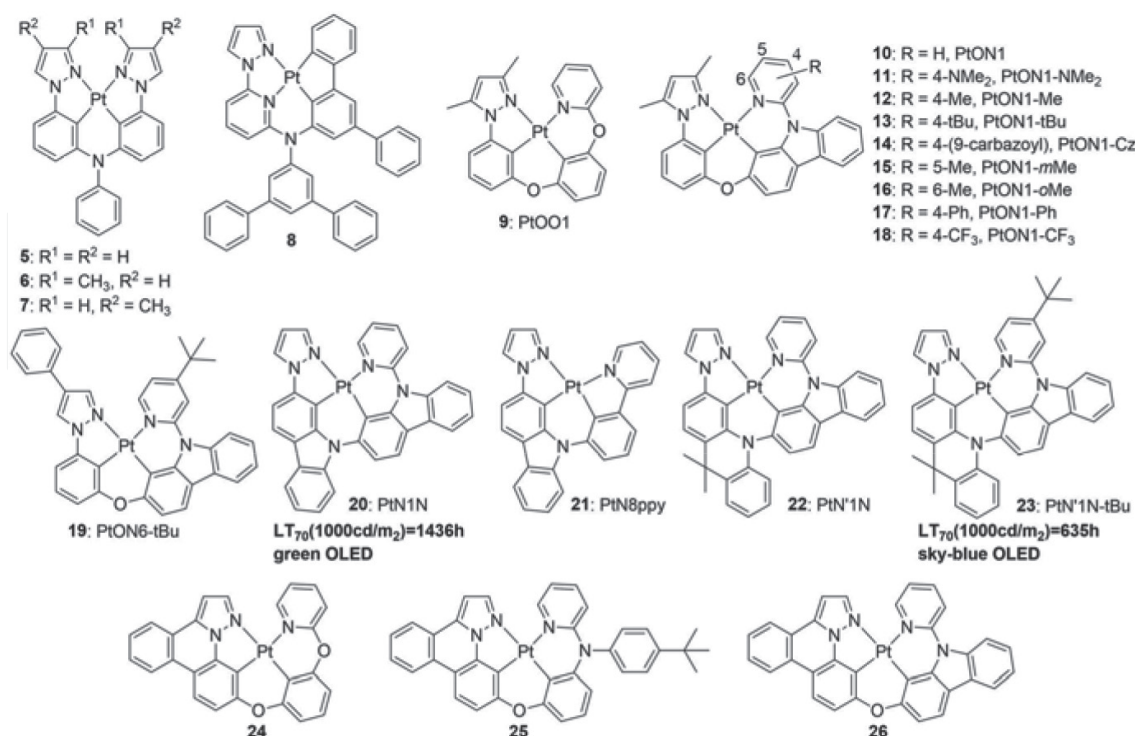


Figure 2. Molecular structures of pyrazole-based tetradentate platinum(II) complexes and operational lifetime of related OLEDs.

blue emitting materials. The photophysical properties and some of the device performances of the pyrazole-based complexes are summarized in **Tables 2** and **3**.

In 2010, Huo et al. reported a series of symmetric tetradentate platinum(II) complexes (**5–7**) containing 1-phenyl-pyrazole moieties [24]. All these complexes emit strongly with ϕ in the range of 37–63%; however, due to the π -conjugation character of the arylamino linking group, their emission energies are relatively low with maximum emission wavelength (λ_{max}) at 474–486 nm in sky-blue and green region. Moreover, excimer emissions were observed for complexes **5** and **7** in solid state peaking at 512 and 516 nm, respectively, because of the strong intermolecular interaction. In 2013, Huo et al. synthesized a 1-(2-pyridinyl)-pyrazole-coordinated complex **8**, which exhibit an even lower emission energy with λ_{max} at 555 nm due to the localization of the first lowest triplet state (T_1) mainly on the biphenyl moiety and the platinum(II) ion [25].

Comp.	In solution at RT					In PMMA at RT		
	Solvent	λ_{max} /nm	FWHM/nm	ϕ /%	$\tau/\mu\text{s}$	λ_{max} /nm	ϕ /%	$\tau/\mu\text{s}$
5 [24]	2-MeTHF	484;512	—	56	4.9	—	—	—
6 [24]	2-MeTHF	474	—	37	3.4	—	—	—
7 [24]	2-MeTHF	486;516	—	63	5.7	—	—	—
8 [25]	CH ₂ Cl ₂	555	—	17	4.4	—	—	—
9 [23]	CH ₂ Cl ₂	430;456	—	39	3.0	—	83	7.5
10 [26]	CH ₂ Cl ₂	454;478	85	71	3.3	449	85	4.5
11 [27]	CH ₂ Cl ₂	442	15	80	13.5	440	88	11.3
12 [27]	CH ₂ Cl ₂	444	20	89	10.0	445	84	7.6
13 [27]	CH ₂ Cl ₂	444	20	95	8.9	445	88	8.8
14 [27]	CH ₂ Cl ₂	496	84	53	1.8	480	64	2.0
15 [27]	CH ₂ Cl ₂	450;476	79	82	3.5	445	84	4.3
16 [27]	CH ₂ Cl ₂	450;478	121	45	3.1	449	78	4.8
17 [27]	CH ₂ Cl ₂	546	95	19	0.8	503	88	2.2
18 [27]	CH ₂ Cl ₂	568	104	1.1	0.6	544	29	0.9
19 [27, 28]	CH ₂ Cl ₂	448	19	—	—	447	81	7.4
20 [29]	CH ₂ Cl ₂	491	18	81	12.9	—	90	—
21 [29]	CH ₂ Cl ₂	573	26	40	3.4	—	—	—
22 [30]	CH ₂ Cl ₂	536	111	—	—	476	—	18.0
23 [30]	CH ₂ Cl ₂	486	46	—	—	476	68	—
24 [31]	CH ₂ Cl ₂	443;471	—	70	—	—	—	—
25 [31]	CH ₂ Cl ₂	449;477	—	24	—	—	—	—
26 [31]	CH ₂ Cl ₂	444;474	—	34	—	—	—	—

Table 2. Photophysical properties of pyrazole-based tetradentate platinum(II) complexes.

Dopant	λ_{\max}/nm	FWHM/nm	CIE	η_{EQE}	
				Peak (%)	100 cd/m ² (%)
6% PtON1(10) ^a [26]	454	46	(0.15, 0.13)	25.2	23.3
2% PtOO1-tBu (13) ^b [28]	448	24	(0.151, 0.098)	5.3	2.7
2% PtON6-tBu (19) ^b [28]	452	30	(0.147, 0.093)	10.9	6.6
7% PtN1N (20) ^c [29]	498	20	(0.15, 0.56)	26.1	25.8
2% PtN8ppy (21) ^b [29]	576	28	(0.53, 0.47)	19.3	16.0
6% PtN'1 N-tBu (23) ^d [30]	490	34	(0.157, 0.491)	17.8	17.3
30% 24 ^e [31]	540	—	(0.33, 0.57)	16.4	—
20% 25 ^e [31]	456	—	(0.18, 0.30)	7.7	—
20% 26 ^e [31]	541	—	(0.35, 0.55)	15.7	—

^aDevice structure: ITO/HATCN/NPD/TAPC/dopant: 26mCPy/DPPS/LiF/Al.

^bDevice structure: ITO/HATCN/NPD/TAPC/dopant: 26mCPy/DPPS/BmPyPB/LiF/Al.

^cDevice structure: PEDOT:PSS/NPD/TAPC/dopant: 26mCPy/DPPS/BmPyPB/LiF/Al.

^dDevice structure: ITO/HATCN/NPD/TrisPCz/dopant:mCBP)/mCBT/BPyTP/Liq/Al.

^eDevice structure: ITO/HATCN/TAPC/TCTA/dopant: 26mCPy(or CBP)/TmPyPB/Liq/Al.

Table 3. Summary of OLED performances of the pyrazole-based tetradentate platinum(II) complexes.

To develop blue or deep-blue emitters, the arylamino liker should be replaced with less-conjugated ones, like oxygen or functionalized carbon groups. Based on this design, PtOO1 (**9**) was synthesized by employing 1-phenyl-3,5-dimethylpyrazole and phenoxy-pyridine (ppy) like oxygen in Li's group in 2013 [23]. The dominant emission peaks of PtOO1 are at 420 nm at 77 K and 430 nm at room temperature (RT). The ϕ is relatively low in solution but can be up to 83% with τ of 7.5 μs in PMMA film. However, excimer emission could not be observed; this could be attributed to the boat-like conformation of the two six-membered rings containing the oxygen liker [23] to prevent intermolecular Pt-Pt bond formation.

In 2013, Li's group developed a new type of tetradentate platinum(II) complex PtON1 (**10**) using 3,5-dimethyl-1-phenylpyrazole and thermally and electrochemically stable pyridinyl-carbazole (PyCz) as ligands linked by an oxygen atom [26]. PtON1 exhibits a peak emission at 440 nm with a full width at half maximum (FWHM) of 6 nm at 77 K. However, at RT, the emission spectrum is dramatically broadened, and the FWHM is up to 85 nm with two emission peaks at 454 and 478 nm, respectively, which attributed to dual emission from both the phenyl-pyrazole and PyCz moieties. The ϕ of PtON1 is much higher than that of PtOO1 in CH_2Cl_2 solution, due to more rigid PyCz moiety. Importantly, PtON1-based blue OLED can achieve a peak external quantum efficiency (EQE) of 25.2% and Commission Internationale de L'Eclairage (CIE) coordinates of (0.15, 0.13) but still short of the "pure" blue CIE coordinates of (0.14, 0.08) designated by the National Television System Committee (NTSC) of the USA in 1931.

To afford deep or "pure" blue emitters, the $\text{CIE}_y \leq 0.1$ is needed. To achieve this goal, narrowband emission is required to eliminate the color contamination from the green region. Through a systemic research work, it was found that the emission from the PyCz ligand could be suppressed

by introducing electron-donating group, like -Me, -tBu, and -NMe₂, to the 4-position of the pyridine ring to increase the energy level of the metal-to-ligand charge-transfer (MLCT) states of the PyCz moiety. Therefore, a series of deep-blue emitters, PtON1-NMe₂, PtON1-Me, and PtON1-tBu (**11–13**), were developed peaking at 442–444 nm with FWHM of 15–20 nm and ϕ not less than 80% in CH₂Cl₂ solution at RT (**Figure 3**) [27]. Moreover, it was also found that the emission color could be easily tuned through changing the substitutions or their positions on the pyridine ring, and all the PtON1 series showed intensive emitting except PtON1-CF₃, especially in PMMA films with ϕ of 29–88% (**Figure 3**) [27]. Furthermore, PtON6-tBu, employing the 4-phenylpyrazole in place of 3,5-dimethylpyrazole in PtON1, was also developed as a deep emitter, which exhibit narrowband emission spectrum peaking at 448 nm in CH₂Cl₂ and FWHM of 20 nm [28]. The emission energy does not decrease significantly owing that the 4-phenyl group and the pyrazole are not coplanar in PtON6-tBu. What is more is that deep-blue OLEDs doped 2% PtON1-tBu or PtON6-tBu could reach peak EQEs of 5.3 or 10.9% with CIE_y < 0.1 [28]. The unsatisfied EQEs are attributed to the high T₁ energy of the deep-blue emitters, making them incompatible with known state-of-the-art host materials. Thus, stable host materials with a high T₁ level are still important for the development of deep-blue OLEDs.

In addition to modifying the cyclometalating ligand, the 1-phenyl-pyrazole ligand can be replaced with low-energy ligand, like pyrazolyl-carbazole, and green emitter PtN1N (**20**) was designed and synthesized in Li's group [29]. PtN1N also gives a very narrow emission spectrum peaking at 491 nm in CH₂Cl₂ solution at RT; the FWHM of 18 nm and Huang-Rhys factor (S_M) of 0.3 for the vibrational transition $\nu_{0,1}$ peak at 525 nm can be achieved. Moreover, one 7% PtN1N-doped device demonstrated a peak EQE of 26.1% and only decreased slightly to 25.8% at a luminance of 100 cd/m². Importantly, employing the nitrogen of the carbazole as linking atom can significantly enhance the chemical and device stability. Therefore, using a known stable device structure, 10% PtN1N-doped green OLED could achieved an operational lifetime at 70% initial luminance, LT₇₀ of 1436 h at 1000 cd/m² with peak EQE of 14.3%, which was estimated nearly 72,000 h at a practical luminance of 100 cd/m². Furthermore, improved

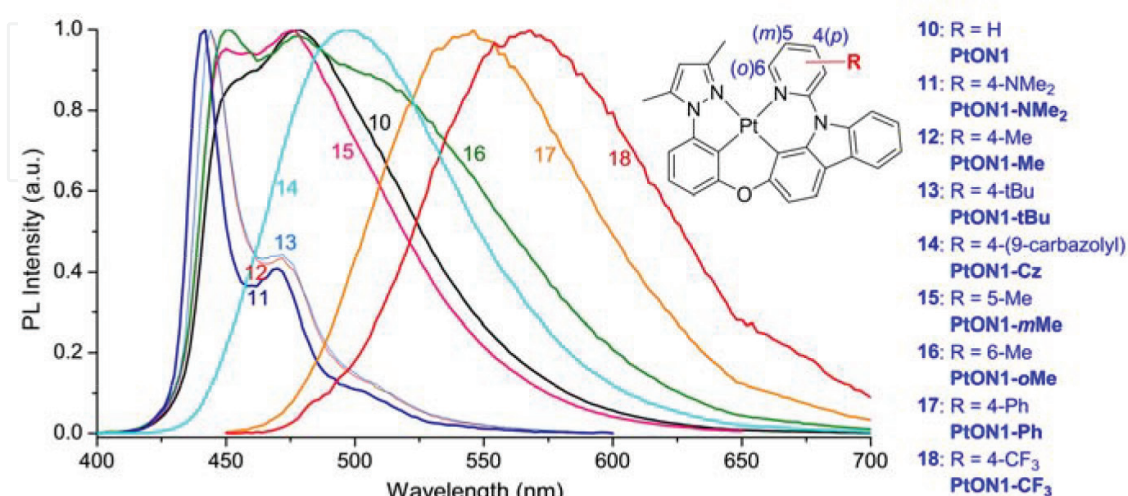


Figure 3. PL spectra comparison of the PtON1 series at RT in CH₂Cl₂ with molecular structures of each emitter inset (adapted with permission) [27].

device by adding an electron-blocking layer (EBL) could achieved peak EQE of 22.1% and still remained 20.3% at 1000 cd/m² with operational lifetime LT₇₀ of nearly 1200 and 60,000 h at 1000 and 100 cd/m², respectively [29]. This device performance is among the highest-efficient green OLEDs reported in literatures. PtN1N also could be employed as an efficient green emitter for the development of white OLED [32]. However, replacing the PyCz for PtN1N with phenylpyridine (ppy) gives an orange emitter PtN8ppy (**21**) because of the localization of the T₁ mainly on the ppy moiety. The peak EQE of a PtN8ppy-based device could also reach close to 20% [29].

The development of efficient and stable blue emitters still maintains a challenge. In order to achieve this goal, chemically and thermally stable ligands must be adopted. Based on the above work, the carbazole in PtN1N was replaced with 9,10-dihydroacridine to break conjugation and increase the T₁ state energy without changing the linking nitrogen atom; therefore, two new tetradentate platinum(II) complexes PtN'1 N (**22**) and PtN'1 N-tBu (**23**) were designed and reported by Li's group recently [30]. Both PtN'1 N and PtN'1 N-tBu show dominant peaks at 476 nm, which blueshifts by 8 nm compared to that of PtN1N in 2-MeTHF at 77 K. Optimized device by employing 10% PtN'1 N-tBu as dopant without EBL could achieve peak EQE of 15.9% and an estimated operational lifetime LT₇₀ of 635 h at an initial luminance of 1000 cd/m² [30]. This device performance is comparable or superior to the best platinum(II)-[33] and iridium(III) [34]-based blue OLEDs reported in literatures [30]. It was believed that the device performance could be further improved if using state-of-the-art host, electron, and hole-blocking materials.

Recently, Fan and Liao et al. designed and synthesized a series of platinum(II) complexes (**24–26**) based on pyrazole[1,5-*f*]phenanthridine-containing ligands [31]. All of them showed high thermal stabilities and strong emission from blue to yellow-green spectral region with ϕ of 24–70%. The dominate emission peaks of all the three complexes are not much difference, but the emission spectra are more and more broad. Interestingly, the emission from PyCz moiety can be observed clearly for complex **26**, which is much like the PtON1 discussed above [27]. Complex **26** demonstrated the best device performance to achieve peak EQE of 16.4%, but unfortunately the operational lifetime of the device was not reported.

4. N-heterocyclic carbene-based tetradentate platinum(II) complexes

Because of the strong δ -donating ability and relatively weak π -accepting property, the N-heterocyclic carbene (NHC) unit could shorten the metal-carbene bond length of the NHC-based platinum(II) complexes, shallow the LUMO energy level to widen the HOMO and LUMO gap, and raise the d-d level of the excited state to suppress the thermally activated nonradiative decay. These will be beneficial for the stability of the complexes and the enhancement of quantum efficiency [12, 17]. Therefore, the NHC-based platinum(II) complexes are appropriate to serve as blue and deep-blue phosphorescent OLEDs. However, due to synthetic challenges and shortage of stable host materials with high T₁ state, the reported NHC-based tetradentate platinum(II) complexes are very rare. Especially, their operational lifetime remains unclear. The NHC-based platinum(II) complexes discussed in this chapter are illustrated in **Figure 4**, their photophysical properties are summarized in **Table 4**, and some of their device performances are illustrated in **Table 5**.

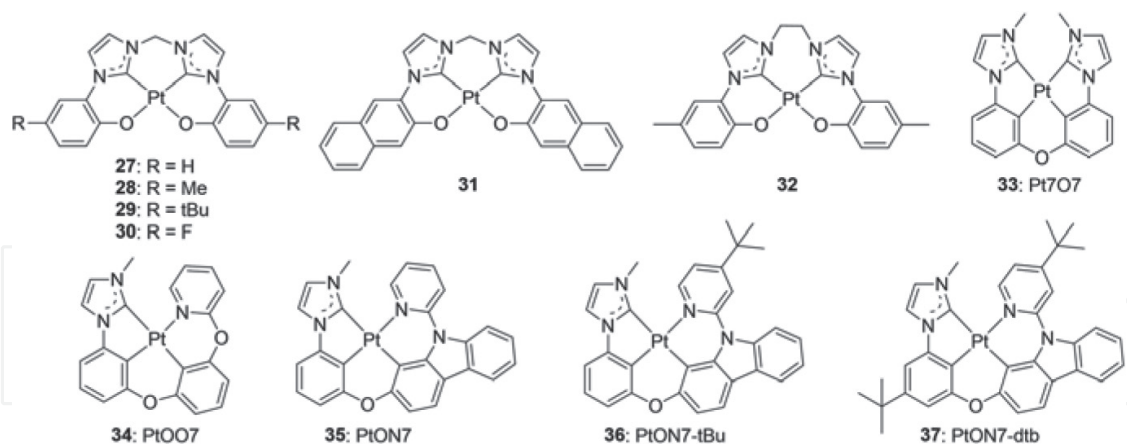


Figure 4. Molecular structures of NHC-based tetradentate platinum(II) complexes.

Comp.	In solution at RT					In PMMA at RT		
	Solvent	$\lambda_{\text{max}}/\text{nm}$	FWHM/nm	$\phi/\%$	$\tau/\mu\text{s}$	$\lambda_{\text{max}}/\text{nm}$	$\phi/\%$	$\tau/\mu\text{s}$
27 [35]	THF-DMF	457	—	3	0.5	443	29	—
28 [35]	THF-DMF	460	—	7	1.8	448	24	—
29 [35]	THF-DMF	461	—	8	1.8	449	26	—
30 [35]	THF-DMF	443	—	18	3.5	434;451	26	—
31 [36]	THF-DMF	531;562	—	15	47.3	—	—	—
32 [36]	CH_2Cl_2	—	—	—	—	480 ^a	—	0.1 ^a
Pt7O7 (33) [37]	CH_2Cl_2	471	20	71	3.2	—	—	—
PtOO7 (34) [26]	CH_2Cl_2	442	66	—	—	442	58	2.5
PtON7 (35) [26]	CH_2Cl_2	452	64	78	4.2	452	89	4.1
PtON7-tBu (36) [29]	CH_2Cl_2	446	20	83	6.6	—	—	—
PtON7-dtb (37) [28]	CH_2Cl_2	446	20	85	5.4	447	91	4.7

^aData were collected in solid state.

Table 4. Photophysical properties of NHC-based tetradentate platinum(II) complexes.

Early in 2011, Che's group had developed a series of symmetric bis-NHC-based platinum(II) complexes by employing $\text{O}^*\text{C}^*\text{C}^*\text{O}$ ligands (27–30, **Figure 4**) [35]. All the four complexes exhibit intense blue phosphorescence either in solutions (ϕ , 3–18%) or in PMMA films (ϕ , 24–29%). Incorporating electron-donating groups into the phenyl rings, like -Me and -tBu, can destabilize the HOMO, resulting in 3–4 nm redshift for the emission spectra of 28 and 29 compared with that of 27. On the other hand, electron-withdrawing group -F can stabilize the HOMO and make a significant blueshift (**Table 4**). Moreover, blue device doped with 28 exhibited emission peak at about 460 nm with CIE coordinates of (0.16, 0.16), but the EQE was low and was not reported. In 2013, Che's group optimized the blue device doped with 4% complex 29, which could achieve a high EQE of about 15% with CIE coordinates of (0.19, 0.21)

Dopant	$\lambda_{\text{max}}/\text{nm}$	FWHM/nm	CIE	η_{EQE}	
				Peak (%)	100 cd/m ² (%)
3% 28 ^a [35]	~460 ^b	~70 ^b	(0.16, 0.16)	—	—
4% 29 ^c [36]	460	~70 ^b	(0.19, 0.21)	~15	
2% Pt7O7(33) ^d [37]	472	20	(0.12, 0.24)	26.3	20.5
14% Pt7O7(33) ^d [37]	—	—	(0.37, 0.42)	25.7	21.5
2% PtOO7 (34) ^e [26]	446	50	(0.15, 0.10)	7.0	4.1
6% PtON7 (35) ^f [26]	458	54	(0.15, 0.14)	23.7	20.4
6% PtON7-tBu (36) ^g [29]	450	28	(0.14, 0.09)	17.6	10.7
2% PtON7-dtb (37) ^g [28]	451	23	(0.146, 0.088)	17.2	12.4
6% PtON7-dtb (37) ^g [28]	452	25	(0.146, 0.091)	19.8	14.7
10% PtON7-dtb (37) ^g [28]	452	39	(0.155, 0.130)	19.6	14.9
14% PtON7-dtb (37) ^g [28]	454	47	(0.161, 0.169)	19.0	15.5
6% PtON7-dtb (37) ^h [28]	451	29	(0.148, 0.079)	24.8	22.7

^aDevice structure: ITO/2-TNATA/NPB/dopant: DP4/TPBi/LiF/Al.

^bEstimated from the EL spectrum in the reported literature.

^cDevice structure: ITO/TAPC/TCTA/CzSi/dopant: CzSi/TmPyPB/LiF/Al.

^dDevice structure: ITO/HATCN/NPD/TAPC/dopant: mCBP/DPPS/BmPyPB/LiF/Al.

^eDevice structure: PEDOT:PSS/NPD/TAPC/dopant: 26mCPy/PO15/LiF/Al.

^fDevice structure: ITO/HATCN/NPD/TAPC/dopant: 26mCPy/DPPS/LiF/Al.

^gDevice structure: ITO/HATCN/NPD/TAPC/dopant: 26mCPy/DPPS/BmPyPB/LiF/Al.

^hDevice structure: ITO/HATCN/NPD/TAPC/dopant: TAPC:PO15/PO15/BmPyPB/LiF/Al.

Table 5. Summary of blue OLED performances of the NHC-based tetradentate platinum(II) complexes.

(**Table 5**) [36]. What’s more is that extended π -conjugation (**31**) or prolonged linking group (**32**) would result in redshift for the emission spectra [36].

In 2014, Li’s group reported a symmetric bis-NHC-based platinum(II) complex Pt7O7 (**33**) by employing C[∧]C[∧]C[∧]C ligands (**Figure 4**) [37]. Pt7O7 exhibits a very narrow emission spectrum peaking at 471 nm with FWHM of only 20 nm in diluted CH₂Cl₂ solution at RT. Two percent of Pt7O7-doped blue device demonstrated a peak EQE of 26.3% and still remained 20.5% at 100 cd/m² with broadening the electroluminescent (EL) spectrum (**Table 4**), paving a new way for the development of efficient blue phosphorescent emitters. Importantly, due to the square planar configuration, excimer would form in elevated concentration, and Pt7O7 could serve as single-doped white OLEDs. The device with the best emitting color could be achieved using a concentration of 14% Pt7O7 with a CRI of 70 and CIE coordinates of (0.37, 0.42), which also exhibited a peak EQE of 25.7%. This was the first reported emitter with both efficient monomer and excimer emissions.

In 2013–2015, Li’s group successively developed a series of blue and deep-blue OLEDs by employing rigid NHC-based platinum(II) complexes, like PtOO7 (**34**), [26] PtON7 (**35**) [26], PtON7-tBu (**36**) [27, 29], and PtON7-dtb (**37**) [27, 28], which adopted asymmetric tetradentate

ligands containing phenoxy-pyridine or pyridinyl-carbazole moieties. All of them exhibit distorted molecular geometry that suppresses the excimer and aggregation formation. PtOO7 shows a broad emission peak at 442 nm in CH₂Cl₂ solution and has a ϕ of 58% and a short τ of 2.5 μ s in PMMA film at RT. As expected, PtOO7-based device exhibited a deep-blue emission with a CIE coordinates of (0.15, 0.10); however, the peak EQE was only 7%, due to its high T₁ state level (2.87 eV) and incompatibility with the host material or improper energy-level alignment inside the emissive layer [16].

On the other hand, all the PtON7 series of complexes (**35–37**) have high ϕ of 78–91% and τ of 4.1–6.6 μ s in solution and PMMA film at RT. Additionally, they have a relatively low T₁ state level (2.81–2.82 eV), allowing them to be compatible with the known and efficient host materials. Encouragingly, PtON7-based device demonstrated a blue color with a CIE coordinates of (0.15, 0.14) and peak EQE of 23.7% still remained 20.4% at 100 cd/m² [26]. However, due to the broad device emission spectrum (FWHM = 54 nm) and significant green emission contamination, the CIE coordinates of (0.15, 0.14) still fail to reach the standard of the “pure” blue coordinates of (0.14, 0.08) [38].

Further modifications are needed for the development of deep-blue OLEDs. Fortunately, incorporating-tBu group into the 4-position of the pyridine ring can elevate the T₁ energy of the pyridinyl-carbazole moiety and suppress its emission, just like the discussion of PtON1 and PtON1-tBu above [27]. Thus, very narrow emission spectra can be obtained for the PtON7-tBu and PtON7-dtb, which have FWHM of only 20 nm, making them suitable for deep-blue emitters (**Figure 5**) [29]. Importantly, the introduction of the other-tBu group to the phenyl ring can significantly enhance the thermal stability of PtON7-dtb and benefit to the high-quality device fabrication. As expected, PtON7-tBu-based device exhibited a deep-blue color and CIE coordinates of (0.14, 0.09) owing to its narrow emission spectrum and also had a peak EQE of 17.6% [29]. What’s more is that PtON7-dtb-based devices demonstrated excellent performances. Increasing the concentration of the PtON7-dtb would broaden the emission spectra; however, no signs of excimer or aggregation formation were observed. Through optimizing the device structure by employing a co-host of hole- and electron-transporting materials, the peak EQE could be further increased to 24.8% and remained 22.7% at practical luminance of 100 cd/m² with a highly desirable CIE coordinates of (0.148, 0.079), very close to the “pure” blue coordinates of (0.14, 0.08) [28]. This device performance is the best for the deep-blue

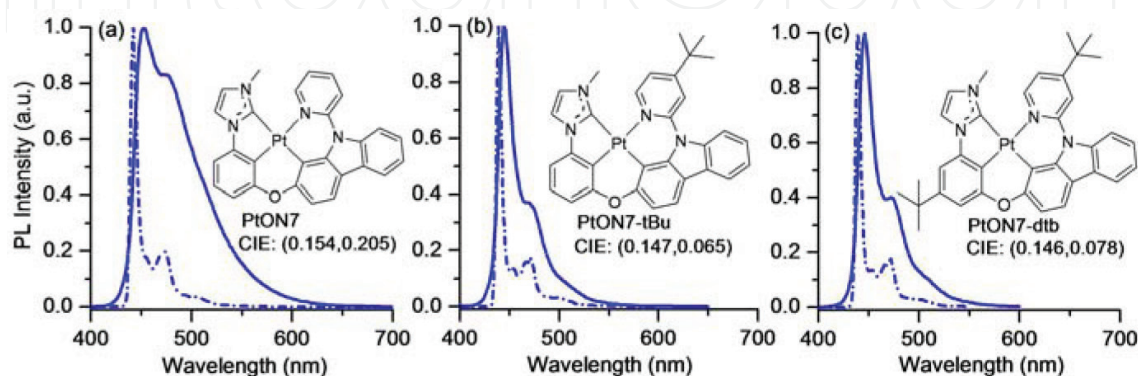


Figure 5. PL spectra of (a) PtON7, (b) PtON7-tBu, and PtON7-dtb at RT in CH₂Cl₂ (solid lines) and 77 K in 2-MeTHF (dash-dotted lines) with molecular structures and CIE coordinates (RT) of each emitter inset (adapted with permission) [27].

phosphorescent OLEDs reported to date [17], and this molecular design by employing asymmetric tetradentate NHC ligands is one of the most successful strategies for the development of deep-blue OLEDs with high color purity. There has also been much progress on the further understanding of the relationship between the molecular modifications and the narrowing of emission band, and research work had been carried out based on the study of the time-dependent density functional theory (TD-DFT), UV, IR, and transient Raman spectra [27, 39, 40].

5. Imidazole-based tetradentate platinum(II) complexes

Compared with the 1-phenyl-pyrazole and phenyl-NHC moieties discussed above, 2-phenylimidazole has a greater degree of π -conjugation and a relatively low T_1 state level. Thus, imidazole-based phosphorescent metal complexes often exhibit redshift and serve as sky-blue emitters. Importantly, they are easily compatible with the known stable host and charger-transporting materials, making them suitable for the development of stable blue OLEDs. Imidazole-based iridium(III) blue emitters have been widely studied and demonstrated high quantum efficiency and impressive operational lifetime, although they are still far from meeting the strict requirements of commercialization [17, 34, 41–44]. However, the reported tetradentate imidazole-based platinum(II) complexes are still rare, which are illustrated in **Figure 6**, their photophysical properties are summarized in **Table 6**, and the device performances are illustrated in **Table 7**.

Interestingly, although adopting different ancillary ligands, PtOO2 (38) and PtON2 (39) nearly have the same T_1 state level, corresponding to their dominant peaks at 462 and 460 nm

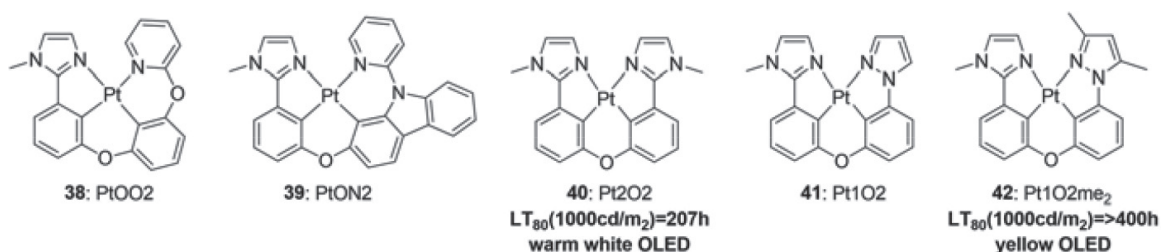


Figure 6. Molecular structures of imidazole-based tetradentate platinum(II) complexes.

Comp.	In CH ₂ Cl ₂ at RT			In PMMA at RT		
	$\lambda_{\text{max}}/\text{nm}$	$\phi/\%$	$\tau/\mu\text{s}$	$\lambda_{\text{max}}/\text{nm}$	$\phi/\%$	$\tau/\mu\text{s}$
PtOO2 (38) [45]	468	64	9.0	—	—	—
PtON2 (39) [45]	466	61	6.5	—	—	—
Pt2O2 (40) [46]	490	—	—	—	84	—
Pt1O2 (41) [46]	474	—	—	—	—	—
Pt1O2me ₂ (42) [46]	470	—	—	—	—	—

Table 6. Photophysical properties of imidazole-based tetradentate platinum(II) complexes.

Dopant	CIE	CRI	η_{EQE}		Device LT ₈₀
			Peak (%)	1000 cd/m ² (%)	1000 cd/m ² (h)
8% PtOO2 (38) ^a [45]	(0.16, 0.34)	—	23.1	15.7	—
8% PtON2 (39) ^a [45]	(0.16, 0.32)	—	22.9	17.5	—
2% Pt2O2 (40) ^b [46]	(0.23, 0.57)	—	25.4	18.2	—
16% Pt2O2 (40) ^b [46]	(0.48, 0.48)	72	24.6	21.0	—
16% Pt2O2 (40) ^c [46]	(0.46, 0.47)	80	12.5	—	207
2% Pt1O2 (41) ^b [46]	(0.22, 0.44)	—	24.1	16.9	—
16% Pt1O2 (41) ^b [46]	(0.49, 0.48)	57	22.6	19.3	—
2% Pt1O2me ₂ (42) ^b [46]	(0.23, 0.44)	—	26.5	17.6	—
16% Pt1O2me ₂ (42) ^b [46]	(0.42, 0.53)	42	24.2	20.6	—
12% Pt1O2me ₂ (42) ^c [46]	(0.43, 0.50)	—	12.3	—	>400

^aDevice structure I: ITO/PEDOT: PSS/NPD/TAPC/dopant:26mCPy/PO15/BmPyPB/LiF/Al.

^bDevice structure II: ITO/HATCN/NPD/TAPC/dopant: 26mCPy/DPPS/BmPyPB/LiF/Al.

^cDevice structure III: ITO/HATCN/NPD/dopant: CBP/BAlq/Alq/LiF/Al.

Table 7. Device performances of pyrazole-based tetradentate platinum(II) complexes.

in 2-MeTHF at 77 K, respectively [45]. Both of them emit strongly in diluted CH₂Cl₂ solution at RT and exhibit λ_{max} at 468 and 466 nm, respectively (**Table 6**). PtOO2- and PtON2-based devices emitted in the blue-green region and demonstrated high peaking EQEs of 23.1 and 22.9% and still could remain 15.7 and 17.5% at 1000 cd/m² in the device structure I (**Table 7**). Due to the P=O, double bond can be irreversibly reduced by electrons in the device to result in the poor electrochemical stability of the hole-blocking material PO15, and the device lifetime was not run in the literature.

Compared with the nonplanar molecular PtOO2 and PtON2, all planar complexes Pt2O2 (**40**), Pt1O2 (**41**), and Pt1O2me₂ (**42**) show redshift, especially for the symmetric Pt2O2, which peaks at 490 nm in diluted CH₂Cl₂ at RT. Importantly, all the three planar complexes have more rigid configuration, which results in strong intermolecular Pt-Pt interaction to form efficient excimers, enabling them suitably for serving as single-doped white OLEDs for lighting application [46]. All the devices doped with either low or high concentrations exhibited very high peak EQEs from 22.6 to 26.5% using the device structure II and could achieve 16.9–21.0% even at 1000 cd/m² (**Table 7**); this device performance indicated that both the monomer and the excimer were highly efficient in the device settings, which were superior to that of the literature reporting bidentate and tridentate platinum(II) complexes, like FPt, Pt-4, and Pt-16 [46]. What's more is that the triplet-triplet annihilation (TTA) processes at high dopant concentrations, which were often observed in the iridium(III)-based devices, were also not significant for these complexes.

The operational lifetime of the devices is one of important parameters for their potential commercialization. Using the stable device structure III, white OLED doped with 16% Pt2O2 demonstrated an operational lifetime LT₈₀ of over 200 h at an initial luminance of 1000 cd/m² with

a color rendering index (CRI) of up to 80 and peak EQE of 12.5% [46]. Due to the strong emission of the excimer, 12% Pt1O2me₂-doped device exhibited a yellow emission; however, the operational lifetime LT₈₀ could achieve over 400 h at an initial luminance of 1000 cd/m², which was twice as long as that of Pt2O2 in the same device setting, and this could be attributed to the lack of high-energy blue emitters in the Pt1O2me₂-based device.

6. Pyridine-based tetradentate platinum(II) complexes

2-Phenylpyridine has been widely used as ligand for the iridium(III)- and platinum(II)-based phosphorescent complexes, like Ir(ppy)₃, due to its high stability and easy preparation. However, owing to the low T₁ state level, the emitting colors are usually from green to red. So far, various types of pyridine-based tetradentate platinum(II) complexes have been reported; importantly, most of them are highly efficient, and some complexes are so stable that they can achieve the early stage of commercial applications. The pyridine-based tetradentate platinum(II) complexes are illustrated in **Figure 7**, their photophysical properties are summarized in **Table 8**, and some of the device performances based on these complexes are showed in **Table 9**.

In 2010, Huo's group reported three pyridine-based platinum complexes (**43–45**) using phenylamine as linking group [24]. Complex **43** exhibits a dominant emission peak at 512 nm in diluted 2-MeTHF solution, and the excimer emission at about 740 nm was observed at elevated concentration, due to the planar molecular configuration. The HOMO level can be stabilized by introducing fluorine atoms into the phenyl rings; thus, complex **44** has a blue-shift of 24 nm with a peaking emission at 488 nm. Because of the electron-donating character of the phenylamine, complex **45** has a shallower HOMO level of −4.56 eV compared to that of complex **43** of −5.27 eV; therefore, significant redshift of 100 nm was observed for complex **45**. All the three complexes show strongly luminescence with ϕ of 14–75% in solution, and device doped with **43** achieved a peak EQE of 14.7% with coordinates of (0.32, 0.62). Unfortunately, the device stability was not studied in the literature.

In 2012, Fukagawa et al. developed two modified complexes TLEC-025 (**46**) and TLEC-027 (**47**) by incorporating δ -donating groups on the phenylamine to further destabilize the HOMO levels, resulting in redshift to about 620 nm, which were ideal emitters for red OLEDs [47]. TLEC-025-based device demonstrated an operational lifetime LT₈₀ of 1290 h with a peak EQE of 18.5% and power efficiency (PE) of 20.7 lm/W at 100 cd/m² and still remained 14.4% and 25.2 lm/W at 1000 cd/m². Encouragingly, device doped with TLEC-027 achieved further long operational lifetime LT₈₀ of 3330 h with similar EQEs and even higher PEs of 25.5 and 30.3 lm/W at 100 and 1000 cd/m², respectively. Unfortunately, the molecular structures of the hole-injecting material ND-1501 and electron-transporting material ETM-143 were unknown. Anyway, this was the first time to demonstrate that the platinum(II)-based devices could be as efficient and stable as the iridium(II)-based ones, opening a door for the development of efficient and stable OLEDs by employing platinum(II) complexes.

Pyridine-based tetradentate platinum(II) complex PtOO3 (**48**) with luminescent quantum efficiency of up to 97% in thin film was developed by Li's group in 2013. PtOO3-based device

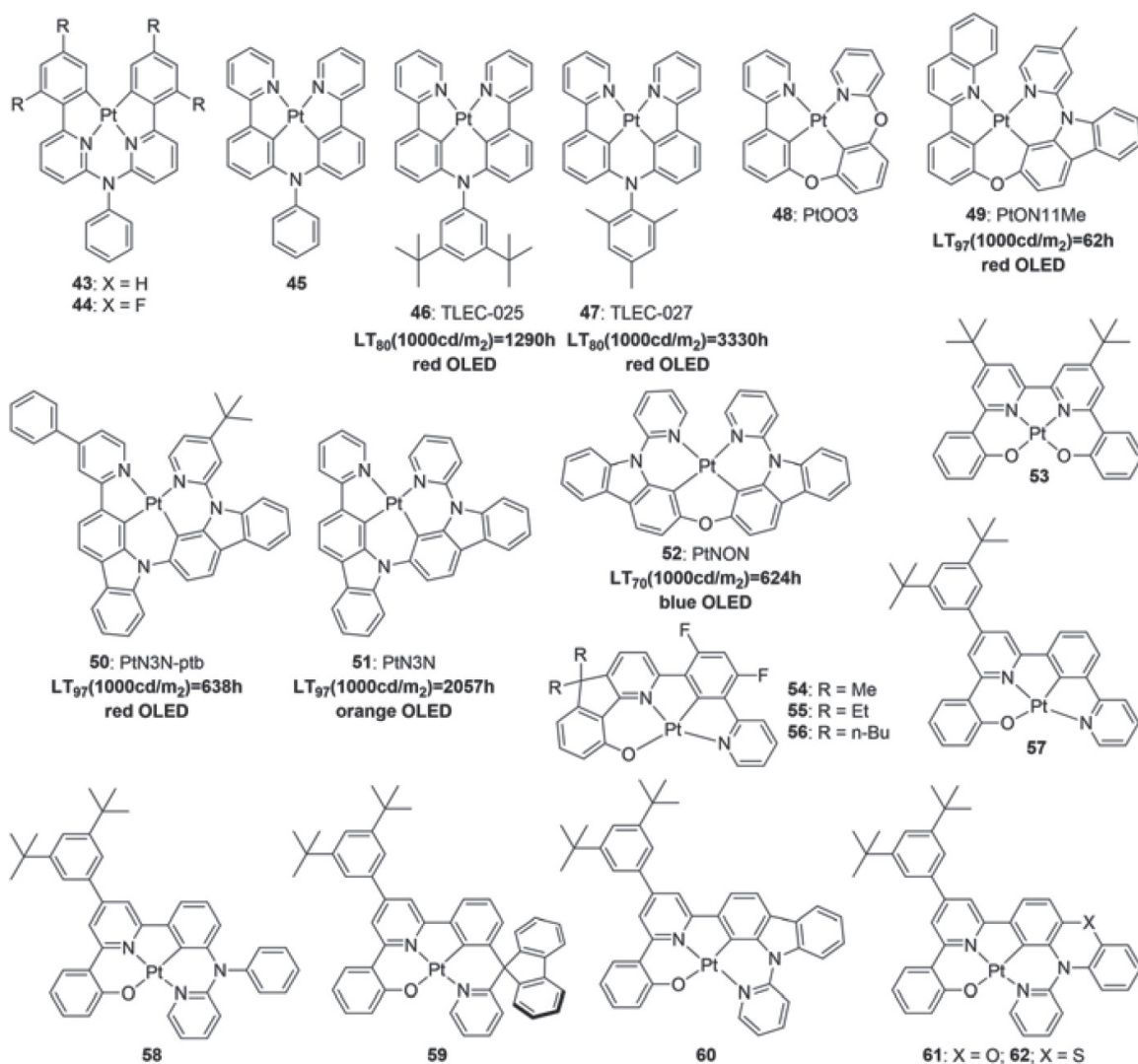


Figure 7. Molecular structures of pyridine-based tetradentate platinum(II) complexes.

performance was compared with that of *fac*-Ir(ppy)₃ in the same device structure, and peak EQE of 22.3% could be achieved [23].

A great progress has been made for the development of stable and efficient platinum(II)-based red OLEDs in the past several years. In 2014, Li's group demonstrated a stable red OLEDs with an estimated operational lifetime LT_{97} of 62 h at 1000 cd/m² with CIE coordinates of (0.60, 0.36) by employing PtON11Me (**49**) as emitter [48]. One year later, tenfold increase in the operational lifetime was achieved using more stable carbazole-linked emitter, PtN3N-ptb (**50**), and an estimated operational lifetime LT_{97} of 638 h at 1000 cd/m² with peak EQE of 10.8%, which used CBP, TrisPCz, and BPyTP as host, electron-blocking, and transporting materials, respectively. Also, the turn on voltage was as low as about 2.0 eV. Moreover, the peak EQE could be increased to 21.5% if using Bebq₂ as host material [49]. What's more is that adopting a bilayer emitting material layer (EML) with different dopant concentrations in the same device structure, PtN3N (**51**)-based orange OLED, could achieve a superior operational lifetime LT_{97} of 2057 h at 1000 cd/m² and peak EQE of 16.9%. This could be attributed to shift the excision formation zone deep into the EML to suppress the potential fast degradation of

Comp.	In solution at RT				In PMMA at RT		
	Solvent	$\lambda_{\text{max}}/\text{nm}$	$\phi/\%$	$\tau/\mu\text{s}$	$\lambda_{\text{max}}/\text{nm}$	$\phi/\%$	$\tau/\mu\text{s}$
43 [24]	2-MeTHF	512, 548	74	7.6	514, 551, 595 ^a	—	—
44 [24]	2-MeTHF	488, 523	75	11.4	541, 583 ^a	—	—
45 [24]	2-MeTHF	613	14	7.6	741, 782 ^a	—	—
46 [47]	—	—	—	—	621 ^b	58	—
47 [47]	—	—	—	—	620 ^{b,c}	—	—
48 [23]	CH ₂ Cl ₂	512	63	2.0	—	97	4.5
49 [48]	CH ₂ Cl ₂	614	—	3.6	—	40	—
50 [49]	CH ₂ Cl ₂	502	34	—	—	—	—
51 [50]	CH ₂ Cl ₂	582	63	7.3	—	—	—
52 [33]	CH ₂ Cl ₂	508	31	2.6	474	83	3.8
53 [51]	CH ₂ Cl ₂	595	12	1.9	—	—	—
54 [52]	CH ₂ Cl ₂	479, 510, 624	60	5.8	—	—	—
55 [52]	CH ₂ Cl ₂	480, 510, 616	66	5.4	—	—	—
56 [52]	CH ₂ Cl ₂	482, 512, 624	75	17.7	—	—	—
57 [52]	CH ₂ Cl ₂	503	76	4.1	—	—	—
58 [53]	CH ₂ Cl ₂	551	90	4.3	—	74	—
59 [53]	CH ₂ Cl ₂	517	80	5.1	—	91	—
60 [54]	CH ₂ Cl ₂	553, 587	86	6.6	—	—	—
61 [54]	CH ₂ Cl ₂	526	47	5.9	—	—	—
62 [54]	CH ₂ Cl ₂	527	49	8.8	—	—	—

^aSolid state.
^bDoped in BeBq₂.
^cEstimated from the emission spectrum.

Table 8. Photophysical properties of pyridine-based tetradentate platinum(II) complexes.

the device [50]. These device performances indicate that the platinum(II)-based complexes are more appealing as phosphorescent emitters in the display applications.

For the development of iridium(III)-based blue emitters containing phenylpyridine moiety, generally, electron-withdrawing groups, like fluorine, are needed to be introduced into the phenyl group to stabilize the HOMO level [21]. However, this would result in electrochemical stability problems to accelerate the device degradation, which was unfavorable to the development of the stable blue OLEDs. In 2016, Li's group developed a new rout for stable and efficient blue OLEDs through breaking the conjugation of the phenylpyridine with a six-membered chelating rings (**52**, PtNON) [33]. Therefore, an operational lifetime LT₇₀ of 624 h at 1000 cd/m² with peak EQE of 10.7% and CIE coordinates of (0.17, 0.32) was achieved for the PtNON-based blue OLED. This device performance was comparable to the best iridium(III)-based blue OLEDs reported in literatures [34].

Dopant	λ_{\max}/nm	CIE	CRI	η_{EQE}		Device LT
				Peak (%)	1000 cd/m^2 (%)	1000 cd/m^2 (h)
4% 43 ^a [24]	512	(0.32, 0.62)	—	14.7	—	—
6% 46 ^b [47]	—	(0.662, 0.337)	—	18.5	14.4	LT ₈₀ : 1920
6% 47 ^b [47]	—	(0.657, 0.342)	—	18.2	14.5	LT ₈₀ : 3330
8% 48 ^c [23]	500	—	—	22.3	17.6	—
6% 49 ^d [48]	—	(0.60, 0.36)	—	4.7	4.6	LT ₉₇ : 62
10% 50 ^e [49]	—	(0.63, 0.37)	—	10.8	7.8	LT ₉₇ : 638
2% 50 ^f [49]	—	(0.58, 0.42)	—	21.5	13.5	LT ₉₇ : 25
10–6% 51 ^g [50]	—	(0.55, 0.45)	—	16.9	15.3	LT ₉₇ : 2057
6% 52 ^h [33]	—	(0.17, 0.32)	—	10.7	9.1	LT ₇₀ : 624
10% 54 ⁱ [52]	—	(0.41, 0.44)	75	11.6	5.5	—
16% 55 ⁱ [52]	—	(0.41, 0.45)	74	17.0	12.4	—
20% 56 ⁱ [52]	—	(0.41, 0.45)	76	9.6	8.4	—
4% 57 ⁱ [52]	—	(0.29, 0.63)	—	9.7	9.5	—
10% 58 ^j [53]	555	(0.44, 0.55)	—	26.0	23.1	—
10% 59 ^j [53]	—	(0.31, 0.64)	—	27.6	25.6	—

^aDevice structure: ITO/CFx/NBP/TCTA/dopant: TPBI:TCTA/TPBI/Alq/LiF/Mg:Ag.

^bDevice structure: ITO/ND-1501/ α -NPD/dopant: Beq₂/ETM-143/LiF/Al.

^cDevice structure: ITO/PEDOT:PSS/TAPC/dopant: 26mCPy/PO15/BmPyPB/LiF/Al.

^dDevice structure: ITO/HATCN/NPD/dopant: mCBP:BAIq/BAIq/Alq/LiF/Al.

^eDevice structure: ITO/HATCN/NPD/TrisPCz/dopant: CBP/BAIq/BPyTP/LiF/Al.

^fDevice structure: ITO/HATCN/NPD/TrisPCz/dopant: Beq₂/BAIq/BPyTP/LiF/Al.

^gDevice structure: ITO/HATCN/NPD/TrisPCz/20 wt%**51**: CBP/6 wt%**51**: CBP/BAIq/BPyTP/LiF/Al.

^hDevice structure: ITO/HATCN/NPD/dopant: mCBP/mCBT/BPyTP/LiF/Al.

ⁱDevice structure: ITO/PEDOT:PSS/dopant: PVK:OXD-7/TmPyPb/TPBi/LiF/Al.

^jDevice structure: ITO/MoO₃/TAPC/dopant: TCTA/TmPyPB/LiF/Al.

Table 9. Device performances of pyridine-based tetradentate platinum(II) complexes.

In fact, a synthetic challenge still remains for the gram-scale preparation of the PtNON and the PtON1 series complexes. Recently, our group developed an efficient approach for the CuCl-catalyzed C-N bond cross coupling of carbazoles and 2-bromopyridine derivatives to synthesize 2-bromo-*N*-(hetero)arylcarbazoles. It was found that base *t*-BuOLi could accelerate the reaction significantly and just a few hours needed to complete the reaction [55]. However, 3–6 days were needed if using K₂CO₃ as base according to the previous reported method [28, 29]. Moreover, a directly hydroxylation of the 2-bromo-*N*-(hetero)arylcarbazoles catalyzed by CuCl was also developed [56]. Both of the approaches are suitable for large-scale synthesis and have been successfully applied in the gram-scale synthesis of PtNON and PdNON, demonstrating its practicability in organic synthesis methodology and materials science [56].

Early in 2013, Che's group had developed a series of symmetric (**53**) [51] and asymmetric (**54–62**) [52–54, 57] phenoxyl-pyridine containing tetradentate platinum(II) complexes. All asymmetric

complexes have high ϕ of 49–90% and τ of 4.1–17.7 μ s in CH_2Cl_2 solutions, and the OLEDs doped these complexes that showed very high brightness, even up to 66,000 cd/m^2 at 10.5 eV. Moreover, the planar rigid molecular configuration enabled the fluorine-containing complexes **54–56** to have strong excimer emission at 616–624 nm, making them serve as ideal emitters for single-doped white OLEDs with CRI of up to 76 [52]. However, after introducing sterically bulky 3,5-di-*tert*-butylphenyl group to the pyridine ring, excimer formation was suppressed for the complexes **57–62**. Devices doped with complex **58** bridging phenylamine or complex **59** with a spiro linkage demonstrated peak EQEs over 25% and maximal PEs up to 109.4 lm/W using TmPyPB as ETL. The maximal PE of complex **59** could further be improved to 126.0 lm/W if Tm3PyBPZ as ETL, which were the highest among the reported platinum(II)-based OLEDs [53]. In the same year, Che's group developed another series of tetradentate platinum(II) complexes containing carbazole (**60**), phenoxazine (**61**), and phenothiazine (**62**) moieties, which served as yellow phosphorescent emitters combined with blue emitter to make white OLEDs [54].

7. Other types of tetradentate platinum(II) complexes

Besides the four series of tetradentate platinum(II) complexes discussed above, there were also some other new types. In 2015, a series of sky-blue emitters based on 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole or 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazole containing spiro-arranged tetradentate ligands were developed. The peak EQE of one blue OLED could reach 15.3% and CIE values of (0.190, 0.342) [58]. In 2017, Liao, Fan, and co-workers developed three 1-isopropyl-2-phenyl-benzo[*d*]imidazole-based emitters with decomposition temperature above 400°C, and one device exhibited a peak EQE of 22.3% [59].

Very recently, Fukagawa and co-workers reported great progress in ultrapure green OLEDs based on a NHC emitter PtN7N [60], which was developed by Li's group before 2014 [61]. The optimized OLED showed CIE coordinates of (0.18, 0.74) using a top-emitting OLED with a microcavity structure and also using a boron-based host material [60]. Fukagawa's work demonstrated that the narrowband emitter PtN7N was superior to the iridium(II)-based emitter $\text{Ir}(\text{mppy})_3$ for the development of ultrapure green emitter to satisfy the BT.2020 for ultrahigh-definition displays [60], owing to the very small vibrational structures of PtN7N that could be well suppressed by microcavity technology. Similar phenomenon was also observed in the previous report of narrowband green emitter PtN1N vs. PtOO3 [62]. Moreover, Fukagawa's work also demonstrated that the operational stability of PtN7N-based OLEDs could be comparable to that of the $\text{Ir}(\text{mppy})_3$ -based ones, indicating the promise for the practical application of PtN7N by employing suitable host and charge-transporting materials [60, 63].

8. Conclusion

In summary, after over 10 years of development, the emission spectra of the tetradentate platinum(II)-based OLEDs can cover the whole visible spectrum, they also exhibit high efficiency, and some show high color purity and long operational lifetime, demonstrating their

potential applications for the next-generation full-color display and solid-state lighting. Owing to the square planar and rigid molecular configurations, platinum(II) complexes have many unique and exciting photophysical properties. On the one hand, easy molecular modification enables tunable emission spectra, and the FWHM of the pyrazole- or NHC-carbene-based complexes can achieve no more than 20 nm and can be as narrow as 15 nm. This facilitates them to serve as efficient deep-blue emitters, and device-doped NHC-carbene-based complex successfully realized “pure” blue emitting with CIE coordinates of (0.148, 0.079) and peak EQE of 24.8%. On the other hand, some planar d⁸ platinum(II) complexes can form intermolecular Pt-Pt bond to achieve 18e structure in their excited state, making them serve as single-doped white OLEDs with high CRI values. Besides, tetradentate platinum(II)-based green, especially for the red OLEDs, demonstrated superlong operational lifetime and satisfied the requirements of the initial commercialization. What’s more is that sky-blue OLEDs also achieved encouraging performances, indicating their bright future for the development of the efficient and stable blue OLEDs.

Despite great progress that has been made for the tetradentate platinum(II) complexes, a challenge remains for the development of the stable deep-blue OLEDs, and more work still be needed. To overcome this challenge, it is important to develop stable host materials with a high enough T₁ state level and highly balanced charge carrier ability. However, through continued efforts of the academia and industry, we believe that these critical issues can be solved and the platinum(II)-based OLEDs will be one candidate for display and lighting applications.

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Abbreviations

Alq ₃	tris(8-hydroxyquinolino)aluminium
BAlq	bis(2-methyl-8-quinolinolato) (biphenyl-4-olato)aluminum
Bebq ₂	bis(benzo[h]quinolin-10-olato-κN,κO)beryllium(II)
BmPyPB	1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene
BPyTP	2,7-di(2,2'-bipyridin-5-yl)triphenylene
CBP	4,4'-bis(<i>N</i> -carbazolyl) biphenyl
CzSi	9-(4-(<i>tert</i> -butyl)phenyl)-3,6-bis(triphenylsilyl)-9 <i>H</i> -carbazole
DPPS	diphenyl-bis[4-(pyridin-3-yl)phenyl]-silane

HATCN	1,4,5,8,9,12-hexaazatriphenylene-hexacarbonitrile
mCBT	9,9'-(2,8-dibenzothiophenediyl)bis-9 <i>H</i> -carbazole
26mCPy	2,6-bis(<i>N</i> -carbazolyl) pyridine
mpy	3-methyl-2-phenylpyridine
2-MeTHF	2-methyltetrahydrofuran
NPD	<i>N,N'</i> -diphenyl- <i>N,N'</i> -bis(1-naphthyl)-1,1'-biphenyl-4,4''-diamine
OXD-7	1,3-bis[(4- <i>tert</i> -butylphenyl)-1,3,4-oxadiazolyl]phenylene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)
PO15	2,8-bis(diphenylphosphoryl)-dibenzothiophene
ppy	2-phenylpyridine
PVK	polyvinylcarbazole
TAPC	di-[4(<i>N,N</i> -ditolylamino)-phenyl]cyclohexane
TCTA	4,4',4''-tris(<i>N</i> -carbazolyl)triphenylamine
2-TNATA	tri(4-(naphthalen-2-yl(phenyl)amino)phenyl)amine
TmPyPB	1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene
Tm3PyBPZ	2,4,6-tris(3-(3-(pyridin-3-yl)phenyl)phenyl)-1,3,5-triazine
TPBi	2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1- <i>H</i> -benzimidazole)
TrisPCz	9,9',9''-triphenyl-9 <i>H</i> ,9' <i>H</i> ,9'' <i>H</i> -3,3':6'3''-tercarbazole

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